Ethanolysis of Kraft lignin to platform chemicals on a MoC_{1-x}/Cu-MgAlO$_z$ catalyst

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ABSTRACT

The complete conversion of Kraft lignin is examined over a MoC_{1-x}/Cu-MgAlO$_z$ catalyst in pure ethanol to give value-added chemicals with small molecular weight, including C_6 alcohols, C_8—C_{10} esters, benzyl alcohols and arenes, without the formation of char or tar. MoC_{1-x}/Cu-MgAlO$_z$ exhibited much higher activity than the previously reported MoC_{1-x}/AC, CuMgAlO$_y$ and Cu-MgAlO$_z$ catalysts and achieved the highest yield of aromatic compounds, 575 mg/g lignin, at 330 °C. The complete cleavage of aryl-O bonds in phenols is observed at temperatures over 300 °C. Furthermore, the MoC_{1-x}/Cu-MgAlO$_z$ catalyst is reusable with a 22.4% loss in the yield of aromatic compounds after 5 cyclic runs.

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1. Introduction

Nowadays, with the depletion of the fossil fuels, biomass as a renewable resource of fuels and chemicals draws worldwide attention. Lignin accounts for 15–30 wt% of non-edible biomass, and is produced in a huge amount in the biosphere of the earth [1]. Lignin has a macromolecular structure composed of phenyl-propane units linked by C—O and C—C bonds, with β-O-4 as the most common linkage [2–4]. Hence, lignin has been shown promising to be used as a resource for the production of aromatic chemicals [5–7]. For centuries, Kraft lignin has been produced in a great amount as the byproduct of pulping process in which cellulosic fiber is separated and utilized to produce paper, while lignin is left in the black liquor as a pollution waste [8,9]. In recent decades, lignin has been isolated from the black liquor due to the environmental concerns, however, still mostly used as a low heating value boiler fuel up to date [10].

Many strategies including hydrolysis [11–15], oxidation [16–21] and reduction [22] have been explored in lignin depolymerization. Among them, reduction is the most exhaustively investigated approach with the existence of hydrogen or a hydrogen donner, e.g. methanol [23–25], ethanol [26] and i-propanol [27], suppressing the condensation of the phenolic intermediates [18,28,29]. Ford and his coworkers decomposed organosolv lignin to cyclohexyl derivatives with a Cu-doped porous metal oxide catalyst in methanol at 300 °C without external hydrogen [23]. However, this approach caused the hydrogenation of aromatic rings. Afterwards, they reported that the same catalyst catalyzes the conversion of eucalyptus wood to a liquid fuel with a 77% conversion and a 71% selectivity to higher alcohols and ethers (HAE), especially the substituted cyclohexyl alcohols and ethers (CAE) in methanol [24]. Song et al. [26] reported the depolymerization of birch wood lignin over a nickel-based catalyst in alcohols, including methanol, ethanol and ethylene glycol under an auto-generated pressure at 200 °C for 6 h. A selectivity to propylguaiacol and propylsyringol as high as 90% was achieved with a lignin conversion of about 50%. Ferrini and Rinaldi [27] reported the catalytic extraction of lignin from poplar wood in 2-Propanol/H_2O (7:3, v/v) with Raney Ni as the catalyst with a 15–26% yield of non-pyrolytic lignin bio-oil containing diols, cyclohexanols, phenols, guaiacols and syringols etc. Volatile components accounted for 55% of the oil sample at 300 °C. Huang et al. [30] investigated the depolymerization of alkali lignin in supercritical ethanol at 300 °C with CuMgAlO$_y$ as the catalyst. A 23 wt% yield of aromatics was achieved without char formation. Earlier to Huang's work, our group reported the catalytic

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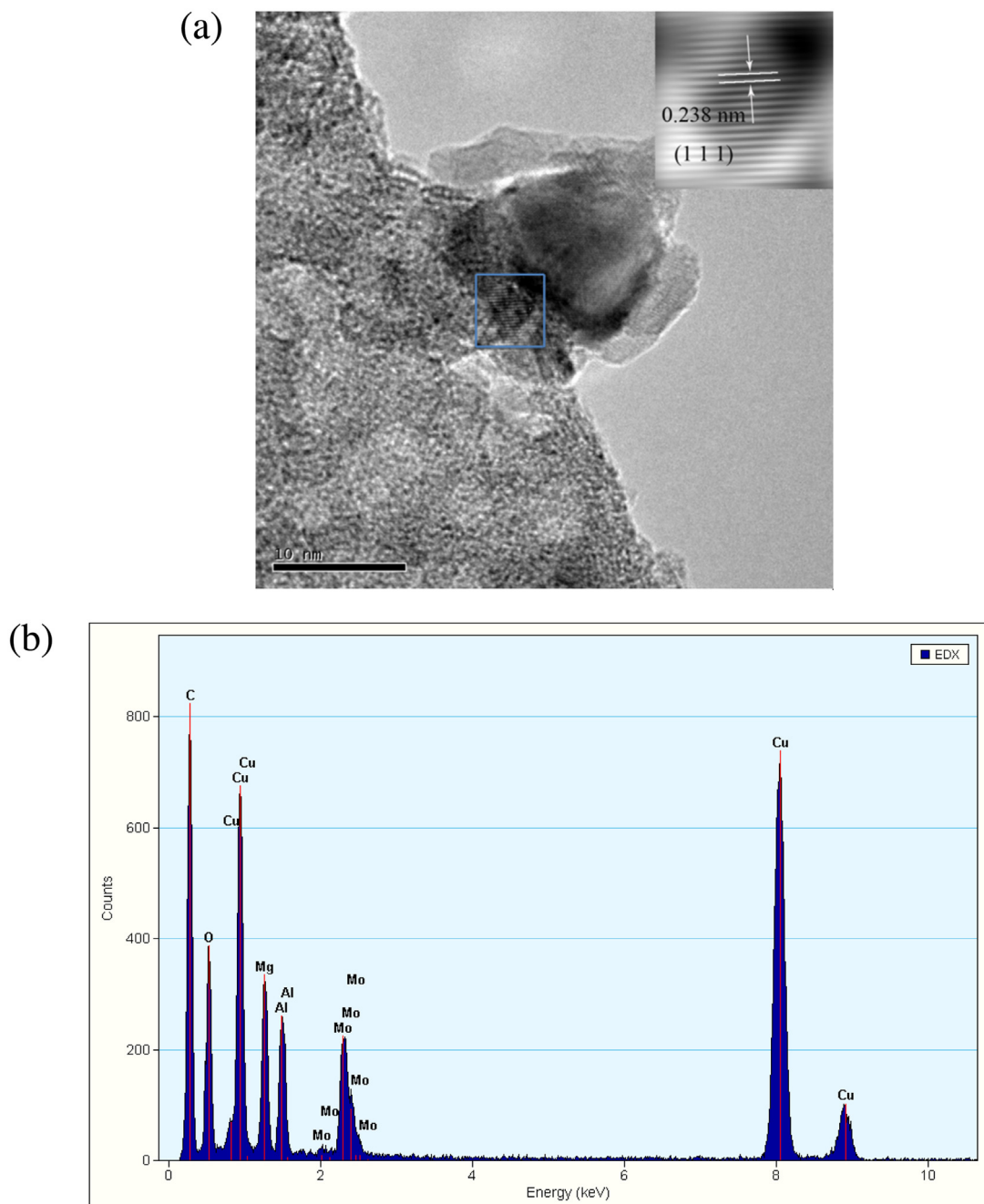*E-mail address:* ydli@tju.edu.cn (Y. Li).

Fig. 1. (a) TEM image of $MoC_{1-x}/Cu-MgAlO_z$, the inset is the framed area after amplification. (b) Energy Dispersive Spectrum (EDS) of $MoC_{1-x}/Cu-MgAlO_z$.

ethanolysis of Kraft lignin with MoC_{1-x}/AC as a catalyst to produce value-added chemicals [31]. Five sorts of products including esters, alcohols, arenes, phenols and benzyl alcohols were obtained with a high overall yield. The selective production of five mono-phenols from Kraft lignin over a tungsten phosphide catalyst in hot compressed water–ethanol mixed solvent was also reported [32]. An activated carbon supported WP gave the highest overall phenols yield, 67.0 mg/g lignin.

In this work, we report the depolymerization of Kraft lignin in supercritical ethanol on a $MoC_{1-x}/Cu-MgAlO_z$ composite catalyst, which is virtually a combination of the reported catalysts of Huang et al. and Ma et al. [30,31] This catalyst gives a much higher yield of products than both the MoC_{1-x}/AC and $CuMgAlO_y$ catalyst, respectively, without any tar or char formation.

2. Experimental

2.1. Materials

The Kraft lignin was purchased from Sigma–Aldrich (product number 471003). The Kraft lignin contains Klason lignin, polysaccharides, extractives (fatty, resin acids and terpenoids), other orgainics and inorganics, with contents of 45.7, 10.1, 4.0, 27.1 and 13.1 wt%, respectively [31]. The elemental contents of the Kraft lignin are 49.5 wt% C, 4.71 wt% H, 0.15 wt% N and 2.80 wt% S, while the ash content is 19.4 wt%. Analytical reagents (AR), including ethanol, o-cresol, ammonium paramolybdate $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, $Cu(NO_3)_2\cdot3H_2O$, $Mg(NO_3)_2\cdot6H_2O$, $Al(NO_3)_3\cdot9H_2O$, NaOH, and Na_2CO_3 were purchased from Tianjin Guangfu Technology Development Co. Ltd. and used as received.
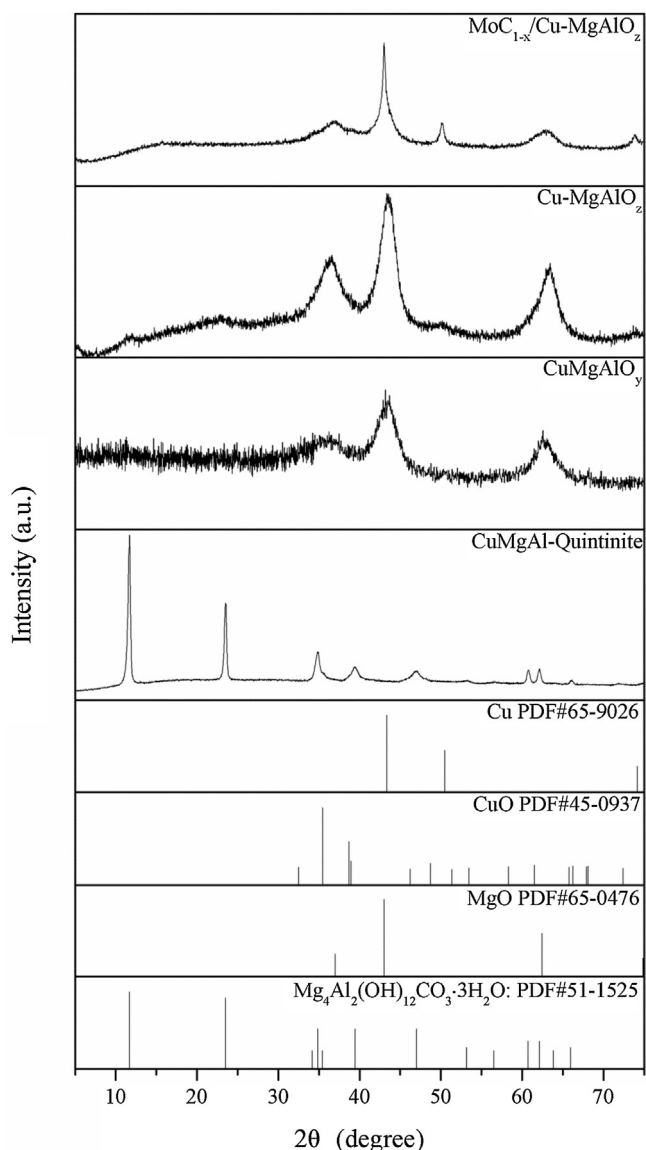
Fig. 2. XRD patterns of MoC_{1-x}/Cu-$MgAlO_z$, Cu-$MgAlO_z$, $CuMgAlO_y$, and CuMgAl-Quintinite.

The water used was provided by an Ultrapure water purification system (UPH-1-10). The gases used in this work include H_2 (99.999 vol%), CH_4 (99.9 vol%), industrial grade nitrogen (99.5 vol%) and N_2 (99.999 vol%). Moreover, air was supplied by an air pump.

2.2. Catalyst preparation and characterization

CuMgAl mixed oxide ($CuMgAlO_y$) was prepared with a co-precipitation method as reported by Huang et al. [30]. $Cu(NO_3)_2 \cdot 3H_2O$ (8.67 g, 0.036 M), $Mg(NO_3)_2 \cdot 6H_2O$ (29.77 g, 0.116 M), and $Al(NO_3)_3 \cdot 9H_2O$ (28.50 g, 0.076 M) were dissolved in 190 mL de-ionized water. The solution, along with 190 mL NaOH (18.24 g, 0.456 M) solution, were slowly added to 285 mL Na_2CO_3 (9.67 g, 0.091 M) solution keeping at 60 °C with vigorous stirring, whilst keeping the pH of the slurry at 10. When the addition was completed, the slurry was aged at 60 °C under stirring for 24 h. The precipitate was filtrated and washed with de-ionized water until the filtrate reached pH 7. The solid was dried overnight at 110 °C, ground and sieved to a particle size below 125 μm, and the material was denoted as CuMgAl-Quintinite. This material was calcined with a heating rate of 2 °C min⁻¹ from 40 °C to 460 °C and

kept at this temperature for 6 h in static air. The resulting material was denoted as $CuMgAlO_y$.

The catalyst MoC_{1-x}/Cu-$MgAlO_z$ was prepared with a temperature programmed reduction procedure. For preparation, 3 g of $CuMgAlO_y$ was incipient-wetness impregnated with an aqueous solution containing 2.37 g of ammonium paramolybdate. The material was dried at 110 °C overnight, ground and sieved to a particle size below 125 μm. This precursor was then exposed to H_2 (40 mL/min, STP), and heated to 350 °C at 5 °C min⁻¹ and held at this temperature for 12 h. The gas was then switched to 40 mL/min CH_4/H_2 (15/85, v/v, STP), and the temperature was increased at a 2.67 °C min⁻¹ rate to 590 °C and then held at this temperature for 2 h. The sample was then cooled to room temperature in 40 mL/min CH_4/H_2 (15/85, v/v, STP).

The as synthesized material denoted as MoC_{1-x}/Cu-$MgAlO_z$ was transferred in H_2 atmosphere to the reaction solvent or passivated in flowing 0.5% O_2/N_2 (industrial grade nitrogen) for 20 h at room temperature before physical characterization.

For the preparation of Cu-$MgAlO_z$, $CuMgAlO_y$ was exposed to H_2 (40 mL/min), and heated to 350 °C at 5 °C min⁻¹ and held at this temperature for 12 h. The gas was then switched to 40 mL/min CH_4/H_2 (15/85, v/v, STP), and the temperature was increased at a 2.67 °C min⁻¹ rate to 590 °C and then held at this temperature for 2 h. The sample was then cooled to room temperature in 15 vol% CH_4/H_2. The as prepared material was denoted as Cu-$MgAlO_z$.

X-ray diffraction (XRD) patterns were obtained at room temperature using a Rigaku D/max 2500 v/pc instrument (Rigaku Corp. Japan) with Cu Kα radiation, 40 kV and 200 mA, at a scanning rate of 3° min⁻¹. JADE5 software was utilized for data analysis. High-resolution transmission electron microscopy (HRTEM) was carried out on a Tecnai G2 F20 (FEI) electron microscope. Samples were ground to a fine powder and dispersed in analytical grade ethanol. The dispersed sample was then placed in an ultrasonic bath for 15 min, before a drop of the suspension was placed on a grid. The grid was positioned in the microscope specimen holder.

2.3. Lignin conversion experiments

The depolymerization reactions were carried out in a 300 mL batch reactor (Parr 4566, made of Hastelloy) equipped with a temperature controller (Parr 4848) and a pressure sensor. In a typical run, 1 g lignin, 0.5 g catalyst and 100 mL ethanol were loaded into the reactor. The reactor was evacuated and purged with high-purity nitrogen for five times. The sealed reactor was then heated to the desired temperature and kept for the desired reaction time. After the reaction, the reactor was cooled down to room temperature.

After releasing the gas, the reaction mixture was filtrated. Internal standard o-cresol was added to the liquid sample before GC analysis. The solid residue was washed with ethanol and water, dried at 110 °C overnight and then weighed.

2.4. Product analysis

The organic phase containing the products was injected neatly into an Agilent 6890-5973 GC–MS system for product qualitative analysis. The product was further analyzed quantitatively with an Agilent 6890 GC equipped with a FID. For both GCs, the working conditions were exactly the same. The oven temperature program was set from an initial temperature of 45 °C to a final temperature of 250 °C at 10 °C min⁻¹, and then held at the final temperature for 2 min. The solvent delay was set as 2 min for MS detector. The columns used in the two GCs were both HP-5 MS capillary column (30 m * 0.25 mm * 0.25 μm). A split ratio of 50 was used for the GC-FID and GC–MS analysis. The mass detector was set to scan the m/z range from 10 to 500. Identification of the compounds was achieved by comparing the mass spectra obtained with those in the system's
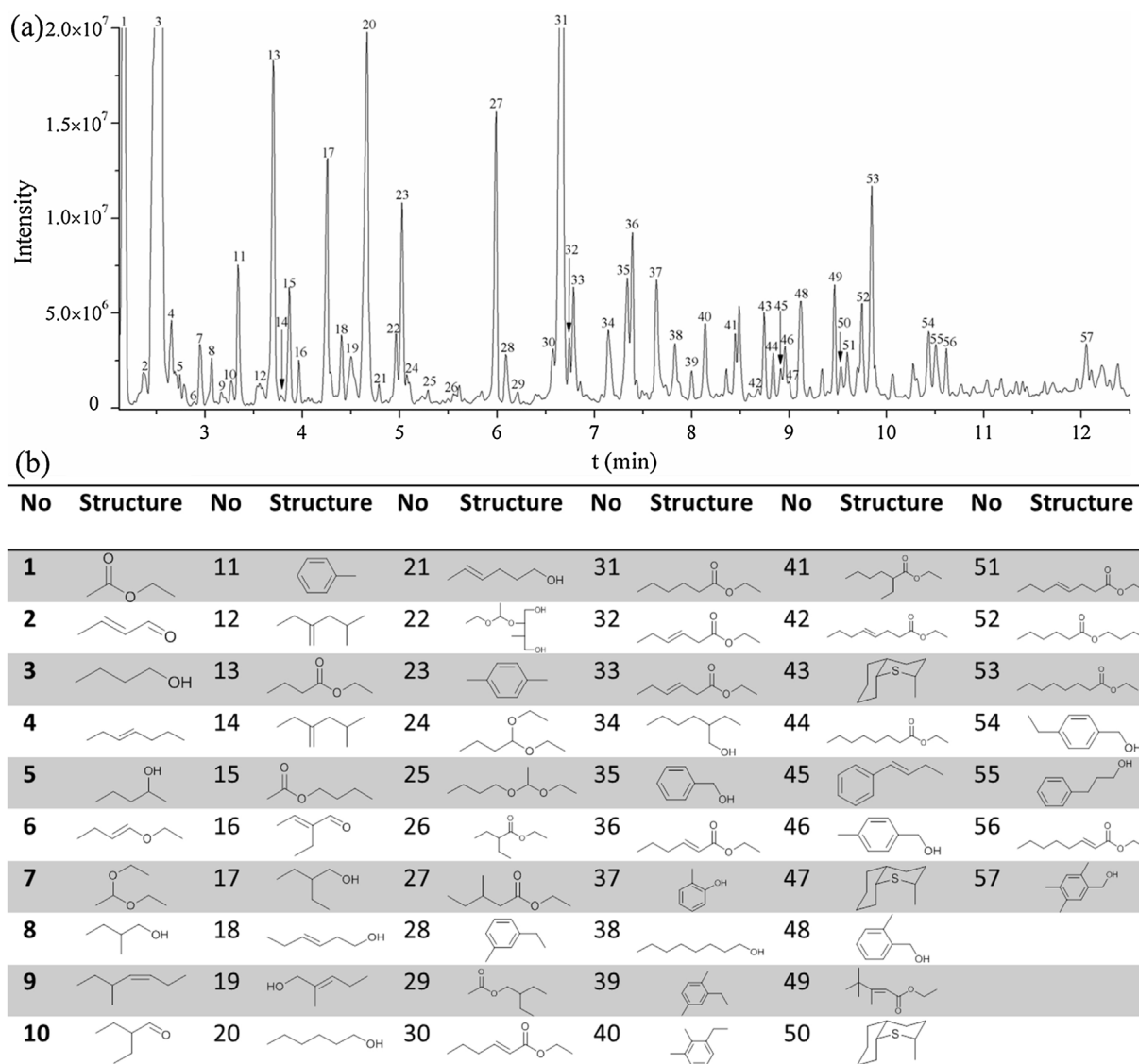
Fig. 3. a) The total-ion chromatogram (TIC) of the liquid product of lignin depolymerization on MoC_{1-x}/Cu-MgAlO$_z$. b) Structures of identified molecules in the liquid product. Note: numbers in the figure and table are the same; O-cresol is the internal standard.

database (NIST02). An internal standard method was performed with the GC-FID to quantify the yield based on the added accurate amount of o-cresol. The calculated product yield was denoted as mg/g lignin.

3. Results and discussion

3.1. Catalyst characterization

The transmission electron microscopy (TEM) of MoC_{1-x}/Cu-MgAlO$_z$ is given in Fig. 1(a). The inset shows the lattice fringe in the framed area with a lattice spacing of 0.238 nm, corresponding to that of the (111) face of α-MoC_{1-x} (JCPDS#15-0457). Energy dispersive spectrum (EDS) of MoC_{1-x}/Cu-MgAlO$_z$ is given in Fig. 1(b) and this spectrum verifies the existence of carbon in the catalyst. The X-ray diffraction (XRD) patterns of CuMgAl-Quintinite, CuMgAlO$_y$, Cu-MgAlO$_z$ and MoC_{1-x}/Cu-MgAlO$_z$ are depicted in Fig. 2. The diffraction pattern of CuMgAl-Quintinite corresponds to that of $Mg_4Al_2(OH)_{12}CO_3\cdot3H_2O$ (JCPDS#51-1525). After calcination at 460 °C, CuMgAl-Quintinite was converted to a mixture of oxides, CuMgAlO$_y$, and the diffraction peaks of CuO (PDF #45-

0937) and MgO (PDF #65-0476) were observed. In the pattern of Cu-MgAlO$_z$, weak peaks of Cu (JCPDS#65-9026) showed up. In addition, the diffraction pattern of CuO (PDF #45-0937) and MgO (PDF #65-0476) still existed, which implied that CuO in CuMgAlO$_y$ was only partially reduced in the temperature programmed reduction process. MoC_{1-x}/Cu-MgAlO$_z$ showed similar pattern to that of Cu-MgAlO$_z$. The difference is that the Cu peaks were stronger and the CuO peak was weaker. MoC_{1-x} in the catalyst didn't show its diffraction pattern because its peaks were weak and close to other diffraction peaks as we previously reported [31]. However, MoC_{1-x} small crystallites were identified in the TEM analysis and the formation of MoC_{1-x} was also supported by EDS.

3.2. Catalytic conversion of lignin

Fig. 3(a) shows the total-ion chromatogram (TIC) of the products of a lignin conversion reaction carried out with MoC_{1-x}/Cu-MgAlO$_z$ as the catalyst at 330 °C for 6 h. A total of 57 compounds are identified by GC–MS and listed in Fig. 3(b). The liquid products mainly include C_4–C_8 alcohols, C_4–C_{10} esters and C_7–C_{10} aromatic compounds. No dimers or oligomers were detected, and no tar or char
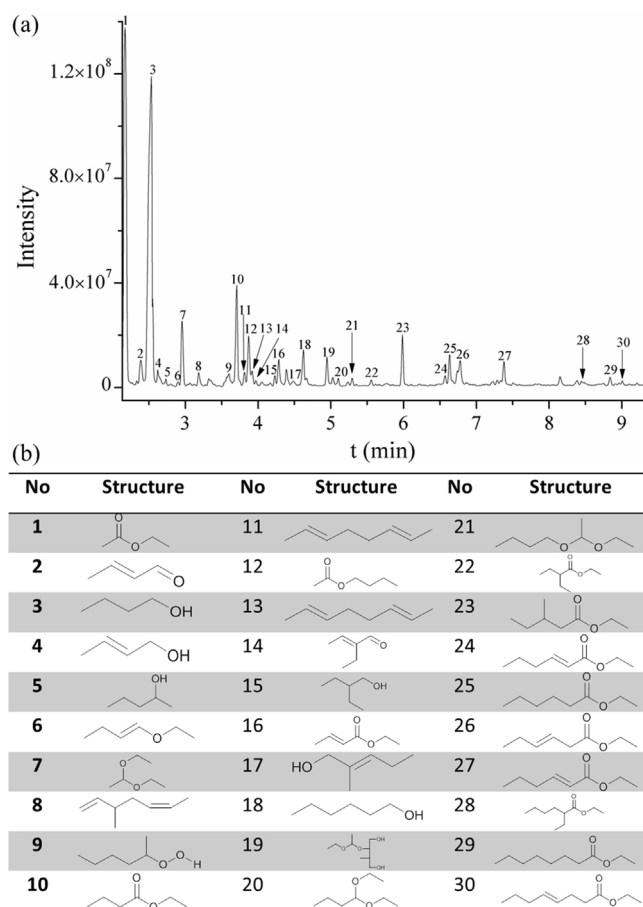
Fig. 4. a) The total-ion chromatogram (TIC) of the liquid product obtained from the blank reaction. b) Structures of identified molecules in the liquid product. Note: numbers in the figure and table are the same.

was formed with this catalyst. A blank reaction was carried out without lignin but with the MoC_{1-x}/Cu-MgAlO$_z$ catalyst and ethanol at 330 °C for 5 h. 30 compounds are identified by GC–MS (Fig. 4(a)). The liquid products mainly contain C_4—C_6 alcohols and C_4—C_{10} esters (Fig. 4(b)). Obviously, C_6 alcohols and C_8—C_{10} esters are formed in the blank reaction without lignin. However, they can also be produced from the conversion of lignocellulosic component. For example, ethyl esters of carboxylic acid can be generated by the esterification reaction between ethanol and lignin-derived intermediates, such as hexenuronic acid formed in Kraft pulping [33]. Furthermore, the alcohols and esters formation were also reported in our previous work and the works done with woody biomass and a copper-doped Mg/Al mixed-oxide catalyst [24,31,34,35]. However, it's hard to determine how much of C_6 alcohols and C_8—C_{10} esters are produced from Kraft lignin. Hence, the yields of C_6 alcohols and C_8—C_{10} esters are listed along with the yield of aromatic compounds but only the latter is considered when discussing the yield of products.

3.3. Roles of components in catalyst

To understand the roles of the different components in the MoC_{1-x}/Cu-MgAlO$_z$ catalyst, the reaction was carried out with CuMgAlO$_y$, Cu-MgAlO$_z$, MoC_{1-x}/AC, the physical mixture of MoC_{1-x}/AC and Cu-MgAlO$_z$, and MoC_{1-x}/Cu-MgAlO$_z$ as the catalyst individually at 300 °C following the same procedure. Similar product distributions were obtained in the reactions with these catalysts, which are also similar as reported previously [31,32].

Fig. 5(a) gives the yields of C_6 alcohols, C_8—C_{10} esters and aromatics obtained on these catalysts. The yields of aromatic compounds achieve 108, 141, 232, 286 and 334 mg/g lignin for CuMgAlO$_y$, Cu-MgAlO$_z$, MoC_{1-x}/AC, the physical mixture of MoC_{1-x}/AC and Cu-MgAlO$_z$, and MoC_{1-x}/Cu-MgAlO$_z$, respectively, while the overall yields of C_6 alcohols and C_8—C_{10} esters are 437, 589, 894, 982 and 1022 mg/g lignin for each catalyst. The amount of solid residue after the reaction with different catalyst is given in Table 1(a). With the increase of the yields of C_6 alcohols, C_8—C_{10} esters and aromatics, the amount of residue keeps decreasing. We then can conclude that: metallic Cu is more active than CuO in catalyzing lignin conversion; MoC_{1-x}/AC shows a better performance than those of CuMgAlO$_y$, Cu-MgAlO$_z$ under the abovementioned conditions; the physical mixing of MoC_{1-x}/AC and Cu-MgAlO$_z$ shows better performance than either of the two component catalysts; the loading of MoC_{1-x} on Cu-MgAlO$_z$ further improved the overall activity of the catalyst, which implies there might be synergistic effects between the two materials. We previously reported that supercritical ethanol on its own degraded Kraft lignin into lignin fragments of intermediate size [31]. In fact, this process might be facilitated by the radicals or ions produced by supercritical ethanol. Fig. 5(b) lists the yields of 7 molecules believed to be produced by the self-reactions of ethanol. These products are produced from ethanol either via a radical pathway or through an ionic pathway. Hence, we propose that a higher yield of the seven ethanol self-reaction products implies a higher concentration of ethanol derived radicals and ions which facilitate the degradation of Kraft lignin into lignin fragments. The yields of the 7 molecules tend to increase in the order CuMgAlO$_y$, Cu-MgAlO$_z$, MoC_{1-x}/AC, the physical mixture of MoC_{1-x}/AC and Cu-MgAlO$_z$, and MoC_{1-x}/Cu-MgAlO$_z$ except that of 2-butenol. Hence, the concentration of lignin fragments should also follow the abovementioned order. That is one of the reasons why the yield of aromatic compounds from lignin conversion follows that order.

3.4. Effect of reaction temperature

The effect of reaction temperature was examined on the MoC_{1-x}/Cu-MgAlO$_z$ catalyst. Fig. 6(a) illustrates the effect of the reaction temperature on the yields of C_6 alcohols, C_8—C_{10} esters and aromatic compounds. From 280 to 330 °C, the yield of C_6 alcohols increased from 101 mg/g lignin to the maximum value of 859 mg/g lignin at 320 °C and then decreased to 704 mg/g lignin at 330 °C. The yield of C_8—C_{10} esters increased monotonically and reached 1928 mg/g lignin at 330 °C, which exceeds the amount of Kraft lignin put into the system. Hence, it's obvious that most esters were formed from ethanol. In contrast, the yield of aromatics increase with the increase of the temperature, however, approaching the maximum value of 575 mg/g lignin, which reflects the limitation of the amount of the lignin in the system. The yield of aromatics is higher than the amount of Klason lignin, 45.7%, which are caused by the alkylation of aromatics. Fig. 6(b) lists the yields of the compounds from ethanol self-reactions. The yields of acetic acid ethyl ester, butanol, ethyl butyrate, butyl acetate and isomerized octenoic acid ethyl ester tend to increase with the increase of temperature, which implies a higher concentration of ethanol derived radicals and ions facilitating the fragmentation of Kraft lignin [35]. That partially explains why the yield of aromatic compounds increases with the temperature. However, the yield of 2-butenol tends to decrease and the yield of 1,1-diethoxyethane fluctuates with the increase of the temperature.

Fig. 7(a) presents the temperature dependence of the yields of the C_6 alcohols in the products. With the increase of the temperature, the yields of hexanol and 2-ethyl-butanol increased to 444 and 240 mg/g lignin as the highest yields respectively at 320 °C and then decreased. The yields of 3-hexenol and 2-methyl-2-pentenol
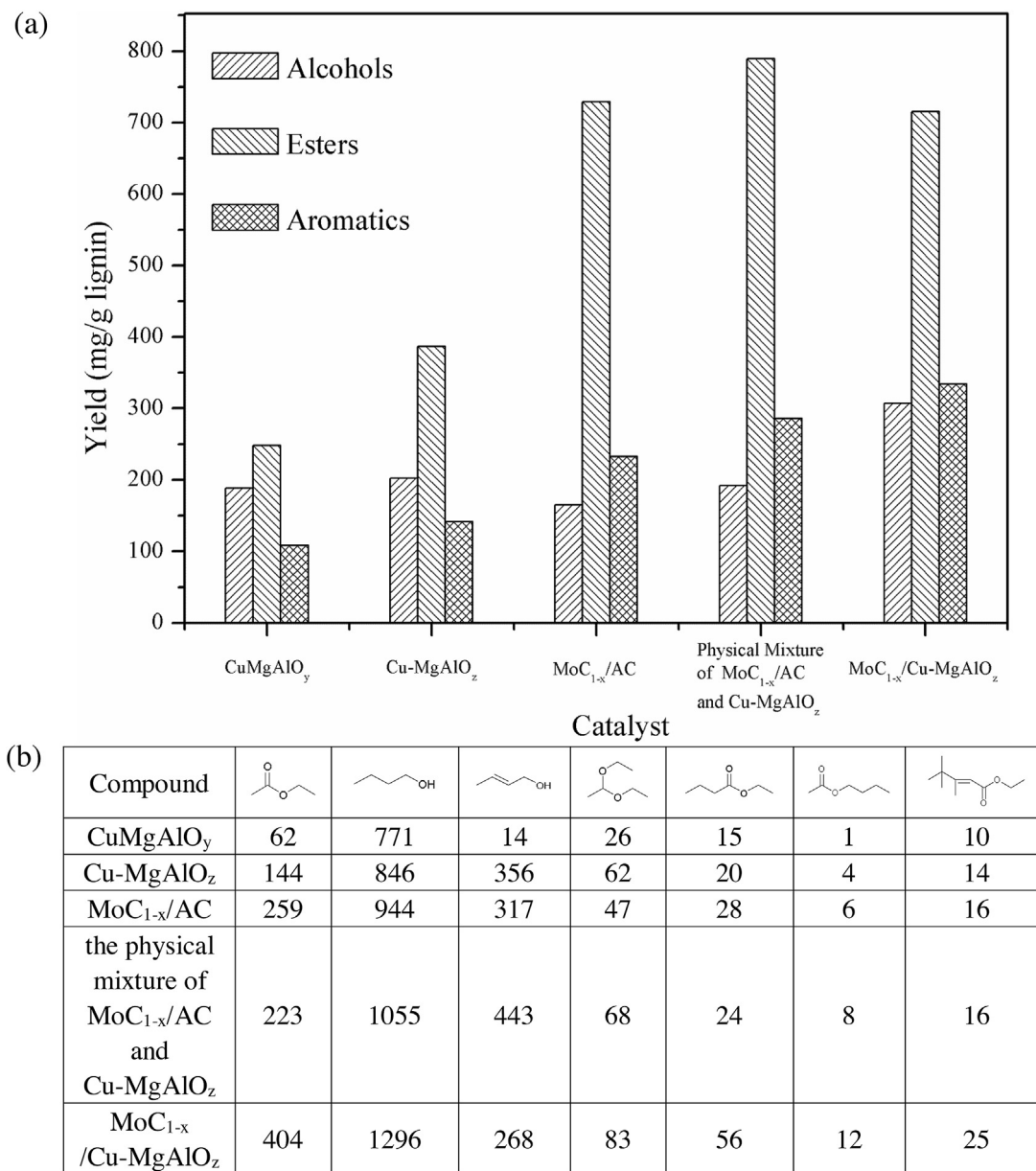
(a)

(b)

Compound	[ester]	[alcohol OH]	[alkene OH]	[diethyl acetal]	[ethyl ester]	[butyl ester]	[branched ethyl ester]
CuMgAlO$_y$	62	771	14	26	15	1	10
Cu-MgAlO$_z$	144	846	356	62	20	4	14
MoC$_{1-x}$/AC	259	944	317	47	28	6	16
the physical mixture of MoC$_{1-x}$/AC and Cu-MgAlO$_z$	223	1055	443	68	24	8	16
MoC$_{1-x}$/Cu-MgAlO$_z$	404	1296	268	83	56	12	25

Fig. 5. (a) The yields of C$_6$ alcohols, C$_8$—C$_{10}$ esters and aromatics in lignin conversion reactions catalyzed by different catalysts. (b) Detailed yields (mg/g lignin) of the products from ethanol self-evolution reactions. Note: the physical mixture of MoC$_{1-x}$/AC and Cu-MgAlO$_z$ includes 0.5 g MoC$_{1-x}$/AC and 0.5 g Cu-MgAlO$_z$.

Table 1
(a) The amount of solid residue after the reaction with different catalyst. Note: the physical mixture of MoC$_{1-x}$/AC and Cu-MgAlO$_z$ includes 0.5 g MoC$_{1-x}$/AC and 0.5 g Cu-MgAlO$_z$. (b) The amount of solid residue after the reaction with MoC$_{1-x}$/Cu-MgAlO$_z$ as a catalyst at different temperatures.

(a)

Catalyst	CuMgAlO$_y$	Cu-MgAlO$_z$	MoC$_{1-x}$/AC	the physical mixture of MoC$_{1-x}$/AC and Cu-MgAlO$_z$	MoC$_{1-x}$/Cu-MgAlO$_z$
Residue/g	1.0672	0.9828	0.8128	1.2587	0.6406

(b)

Temperature/°C	280	290	300	310	320	330
Residue/g	1.0036	0.8307	0.6406	0.5447	0.5303	0.4932

increased slowly with the increase of the temperature and showed fluctuation. The highest overall yield of C$_6$ alcohols being 859 mg/g lignin was achieved at 320 °C. Fig. 7(b) gives the yields of the C$_8$–C$_{10}$ esters as the functions of the reaction temperature. The yield of hex-

anoic acid ethyl ester increased dramatically from 18 mg/g lignin of 280 °C to 802 mg/g lignin of 330 °C as the temperature increased. With the increase of the temperature, the yields of 2-hexenoic acid ethyl ester and 3-hexenoic acid ethyl ester kept relatively stable at
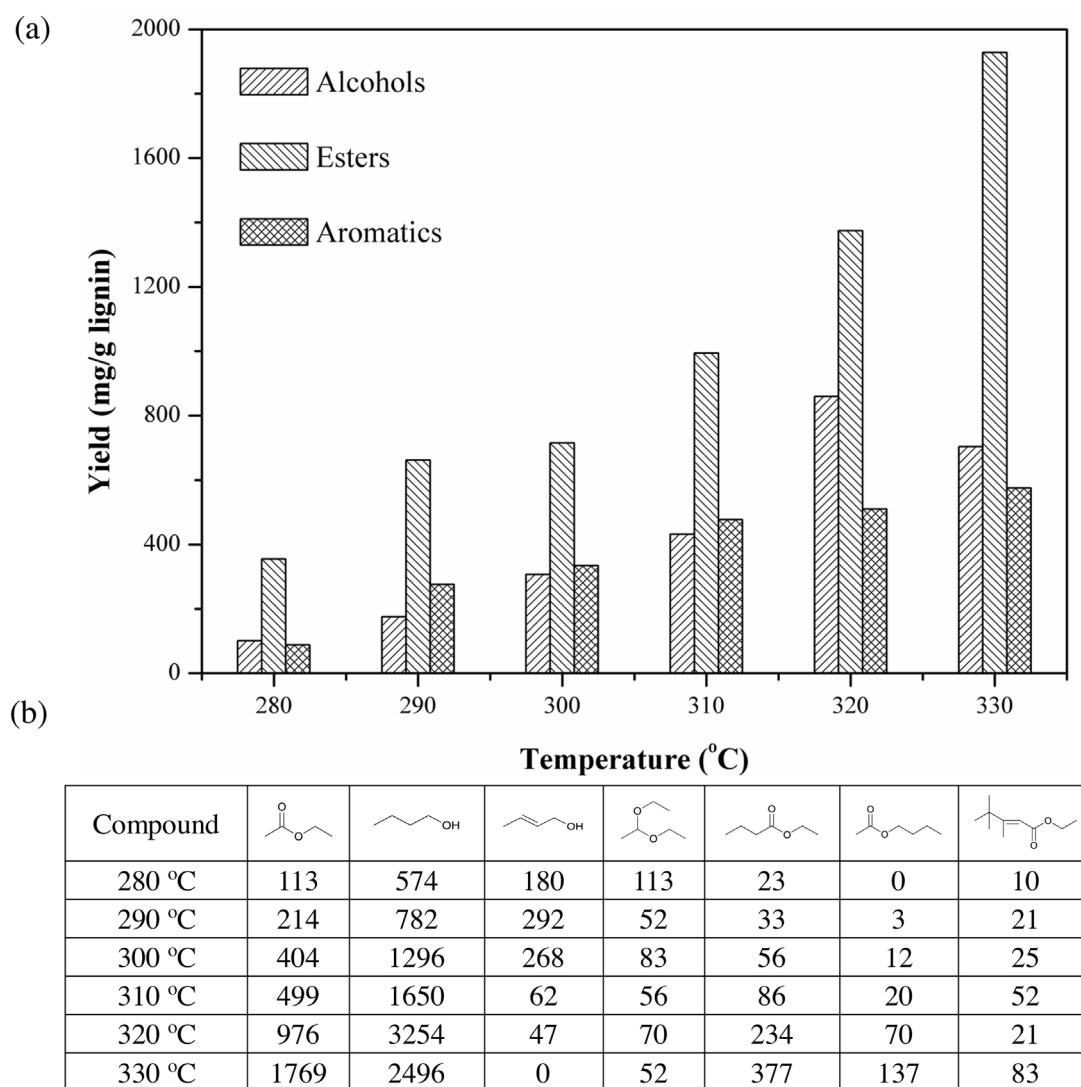
Fig. 6. (a) The influence of temperature on the yields of C_6 alcohols, C_8–C_{10} esters and aromatics over the MoC_{1-x}/Cu-MgAlO$_z$ catalyst. (b) Detailed yields (mg/g lignin) of the products from ethanol self-evolution reactions.

about 200 mg/g lignin and the yields of 3-methyl-valeric acid ethyl ester and octanoic or octenoic acid ethyl ester increased slowly to about 250 mg/g lignin. The highest overall yield of C_8–C_{10} esters being 1928 mg/g lignin was achieved at 330 °C. The overall yield of C_6 alcohols and C_8–C_{10} esters being 2632 mg/g lignin was achieved at 330 °C. The yield of these products far exceeded the amount of the initial Kraft lignin, which was reasonable since ethanol can also produce these products. As shown in Fig. 7(c), with the increase of the temperature from 280 °C to 330 °C, the overall yield of arenes increased from 73 to 319 mg/g lignin while the overall yield of benzyl alcohols increased from 9 mg to 257 mg/g lignin. Interestingly, the yield of phenols increased at first, reached the maximum value of 16 mg/g lignin at 290 °C, and then decreased with the further increase of the temperature. In this reaction, phenols are produced from lignin deploymerization and consumed likely by the deoxygenation, ethoxylation and ethylation reactions. At temperatures lower than 290 °C, the rate of phenols production is higher and increases faster than that of the reactions consuming phenols so the yield of phenols increased when the temperature increased from 280 to 290 °C. However, as the temperature further increased, the rate of the phenol consuming reactions increase faster than

that of phenols production reactions, so that the yield of phenols decreased. The detailed yields of aromatic compounds achieved at 330 °C are listed in Fig. 7(d).

In our previous work, a MoC_{1-x}/AC catalyst showed the best performance at 280 °C with an overall yield of aromatic compounds of 280 mg/g lignin [31]. Here, the overall yield of aromatics on the MoC_{1-x}/Cu-MgAlO$_z$ catalyst is relatively poor at 280 °C. Yet, when the temperature increased, the overall yield of aromatic compounds increased and far exceeded the highest overall yield of the MoC_{1-x}/AC catalyst. The overall yield of the aromatics here with the MoC_{1-x}/Cu-MgAlO$_z$ catalyst reaches 575 mg/g lignin, which is also higher than the yield of monomers, 230 mg/g lignin, obtained with CuMgAlO$_y$ reported by Huang et al. [30]. The new catalyst gave a much higher overall yield than those reported results with MoC_{1-x} and Cu-MgAlO$_z$ catalysts, which implies a synergistic effect between the two materials. Compared to Cu-MgAlO$_z$, a heterogeneous catalyst, MoC_{1-x}/Cu-MgAlO$_z$ can form molybdenum ethoxide (Mo(OEt)$_5$) during the reaction in ethanol as we previously reported [35], which is a homogeneous catalyst so that MoC_{1-x}/Cu-MgAlO$_z$ functions as both homogeneous and heterogeneous catalysts simultaneously. Hence, more radicals and ions were
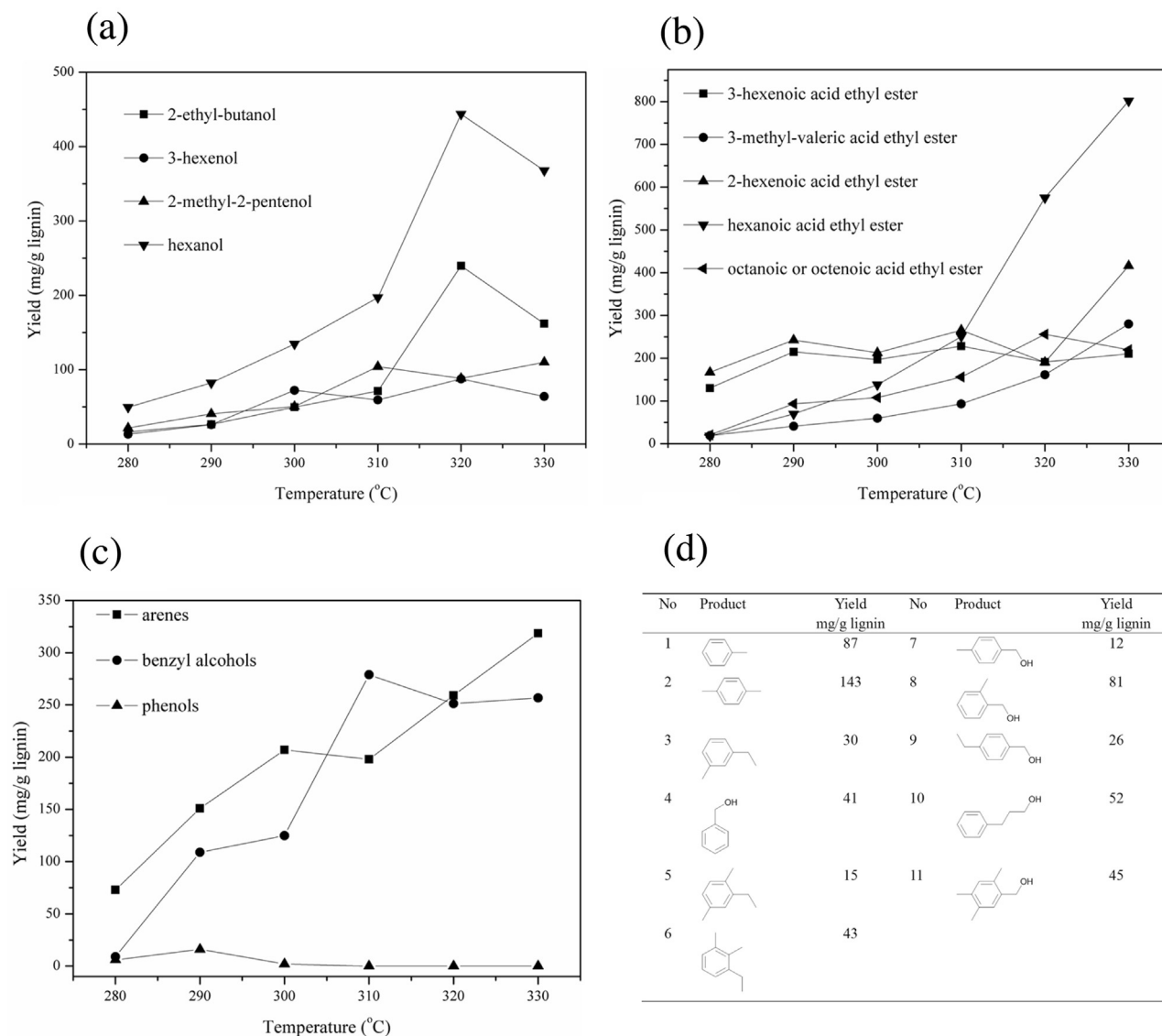
(a)

(b)

(c)

(d)

Fig. 7. (a) Yields of 4 richest C_6 alcohols in lignin ethanolysis reaction catalyzed by MoC_{1-x}/Cu-MgAlO$_z$ at different temperatures. (b) Yields of the 5 richest C_8—C_{10} esters in lignin conversion reaction catalyzed by MoC_{1-x}/Cu-MgAlO$_z$ at different temperatures. Note: the octanoic or octenoic acid ethyl esters include 4-octenoic acid ethyl ester, 3-octenoic acid ethyl ester, 2-octenoic acid ethyl ester and octanoic acid ethyl ester. (c)Yields of aromatic compounds in lignin conversion reaction catalyzed by MoC_{1-x}/Cu-MgAlO$_z$ at different temperatures. (d) Aromatic products and their yields achieved at 330 °C.

formed from ethanol with the MoC_{1-x}/Cu-MgAlO$_z$ catalyst than that with Cu-MgAlO$_z$ as the catalyst. These radicals and ions facilitate the ethanolysis of Kraft lignin into small lignin fragments, so that when MoC_{1-x}/Cu-MgAlO$_z$ catalyst is used, the system has a higher lignin fragment concentration. Cu-MgAlO$_z$, itself, can catalyze the depolymerization of lignin fragments to monomers but the yield is low because it is a heterogeneous catalyst. In the reaction system presented here, Mo(OEt)$_5$, MoC_{1-x} and Cu-MgAlO$_z$ together catalyze the depolymerization of lignin fragments both homogeneously and heterogeneously in MoC_{1-x}/Cu-MgAlO$_z$ catalyzed reaction. Hence, a much higher yield of monomers was achieved on MoC_{1-x}/Cu-MgAlO$_z$. Higher temperature also favors the overall yield of aromatic compounds because it favors the formation of radicals and ions from ethanol, thus facilitate the fractionation of lignin.

The solid residues of the reaction were quantified after filtration, washing with ethanol and water and drying. The results are listed in Table 1(b). When the reaction temperature is increased, the

amount of solid residue decreased monotonically. That is consistent with the increase of the yield of the aromatic products. At 330 °C, the amount of the solid residue was almost the same as that of the fresh catalyst before reaction, which means the complete conversion of the Kraft lignin. Since aromatic compounds only account for 575 mg/g lignin at this temperature, the rest organic components in lignin might have been converted to C_6 alcohols and C_8—C_{10} esters.

3.5. Recyclability of the catalyst

The catalyst was readily separated from the liquid products by filtration, and was directly reused in the successive runs. Fig. 8 shows the results of the reusability tests of the catalyst. The yield of C_6 alcohols decreased greatly in the second run by 35.9% and then recovered gradually. The yield in the fifth run was even a little higher than that in the first run by 0.9%. The yields of C_8—C_{10} esters fluctuated with the increase of the recycles but tended to go down slightly on the whole with 6.3% loss after 5 runs. The yields of aro-
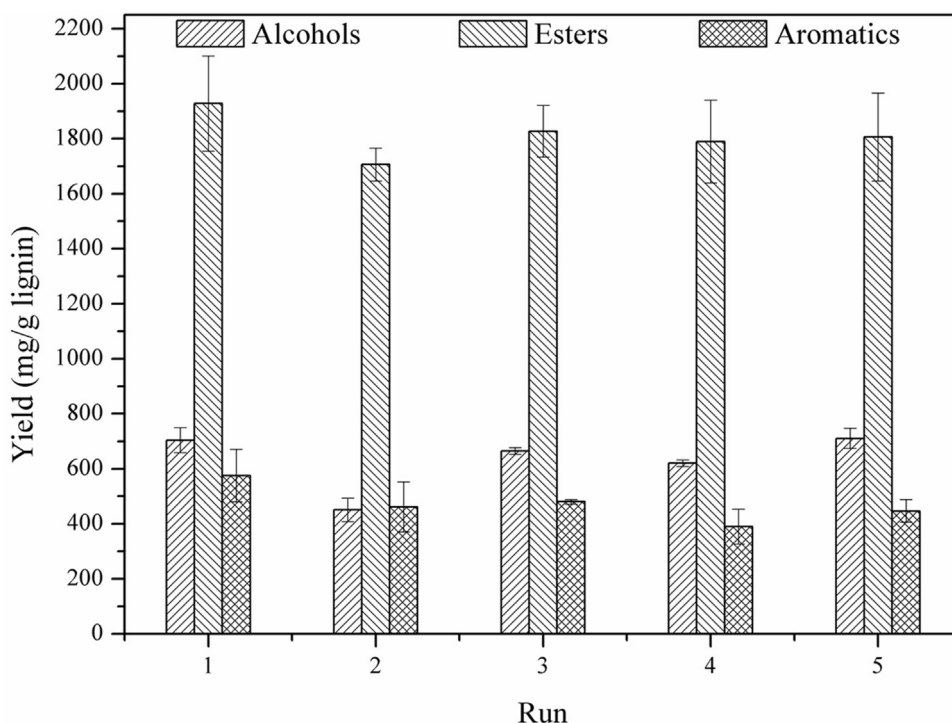
Fig. 8. Recyclablity of MoC_{1-x}/Cu-MgAlO$_z$ catalyst for the conversion of lignin in supercritical ethanol at 330 °C for 6 h.

matic compounds also fluctuated with the increase of the recycles and decreased by 22.4% after 5 runs. Hence, the catalyst can be used at least for five successive runs.

4. Conclusions

Kraft lignin was completely converted to value-added chemicals with small molecular weight, including C_6 alcohols, C_8—C_{10} esters, benzyl alcohols and arenes, over a MoC_{1-x}/Cu-MgAlO$_z$ catalyst in supercritical ethanol. The highest yield of aromatic compounds of 575 mg/g lignin was achieved at 330 °C. Similar product distributions were obtained in the reactions with CuMgAlO$_y$, Cu-MgAlO$_z$, MoC_{1-x}/AC and MoC_{1-x}/Cu-MgAlO$_z$, respectively. However, the yield of aromatic compounds with MoC_{1-x}/Cu-MgAlO$_z$ exceeds those of CuMgAlO$_y$, Cu-MgAlO$_z$ and MoC_{1-x}/AC. The catalyst could be used at least five successive runs with a 22.4% loss in the yield of aromatic compounds.

Acknowledgements

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